Chapter 6

Coupling of angular momenta – the vector model

In the previous chapter, we introduced the central-field approximation as a way to obtain separable basis functions for the states of multielectron atoms. These product states are solution to a Schrödinger equation with a purely radial potential, and they are annotated with an electron orbital nomenclature (see chapters 1.5 and 5.2.1). What we need to do now is to apply perturbation theory, using these electron configurations as zeroth-order functions.

When we initially introduced the CFA in chapter 5, and established electron configurations, we ignored two contributions to the total Hamiltonian; namely the spin-orbit interaction and what's left of the mutual electron repulsion term, when we have separated out its radial part. The issue now at hand is to add these contributions as perturbations. Eventually, we will then be able to further add other interactions, for example with external fields and electromagnetic moments from the nucleus.

What we have to deal with presently is interactions between the orbital and spin angular momenta of *all* electrons. A model for doing this was developed by early spectroscopists, before quantum mechanics and before the salient features of atomic structure were known. It is a phenomenological model based on the addition of vectors, describing the different angular momenta, with constraints concerning the discrete nature of the vector sums. The latter rules was initially entirely based on empirical observations.

When studying atomic spectra, it was noted that groups of of energy levels (derived from spectral lines) appeared together, and that some specific types of atoms always had such groupings with particular multiplicities. For example, alkali atoms had states appearing in doublets, alkaline earths were shown to have singlets and triplets, and nitrogen had its energy levels arranged in quartets and doublets. Working backwards, it was hypothesised that this has to do with interacting angular momenta, and that spin had to be included in the treaties. The model was developed before quantum mechanics, but it turns out that when the addition of angular momenta was subsequently put on a quantum mechanical footing, this vector model still gave excellent qualitative results, and it still greatly facilitates a close study of basic atomic structure and atomic spectroscopy.

In the following, we will introduce the vector model, and we will quickly proceed to the application of quantum mechanical perturbation analyses of the same issue. When doing this, we will have to isolate special cases, where some interactions dominate over others. The extremes of these special cases are the so called *LS*-coupling and jj-coupling schemes. They will be introduced in chapters 6.3 and 6.4, and then treated in detail in chapters 7 and 8. Albeit the above schemes are limiting cases, they will help us to understand a majority of atomic structure, and via interpolation schemes, we can get a good grasp also of various intermediated situations.

6.1 The concept of the vectormodel

The central-field approximation is a key to the justification of the vector model. In the pre-quantum era, and after the introduction of the atomic models by Rutherford and Bohr, the formulation was rather along the lines that only a few of the negative charges in an atom contribute to the finer features of atomic structures. With an atomic model based on discrete orbitals, this could also be stated as that only electron in the outermost occupied orbitals give angular contributions to the structure, whereas the inner ones give a spherically symmetric contribution to the overall energy of the atom. This hypothesis was for early spectroscopists a postulate based on observations. Today, we can give rational arguments for it, and we will dwell on it more in chapter 6.2.

A purely central potential gives a comparatively simple solution to the Schrödinger equation. The observation that atomic spectra can still be very complicated must then lead to the conclusion that these complications have to to with atoms outside the symmetric closed shells, i.e. the valence electrons. Inner, fully occupied orbitals, may combine to a spherical force field, but the remaining valence electrons will exert torques on each other. From there, we can understand that the number of valence electrons must have an important bearing on the energy level structure, and thus it is understandable why atoms found in the same column in the periodic system have similar spectra.

The said angular effects must, from a Newtonian point of view, be possible to describe as interactions between different angular momenta that have the effect that they will all vary with time, whereas their sum will remain constant (for the moment we rule out dissipation). We have

$$\frac{d\mathbf{L}}{dt} = \tau \,, \tag{6.1}$$

and if we take the example of the angular part of the electrostatic interaction between two valence electrons, it is clear that neither L_1, nor L_2 will be constant in time. They will both precess about their vector sum, as illustrated in fig 6.1

In quantum mechanical language, $\mathbf{L}_1^2$ and $\mathbf{L}_1^2$ will commute with $\mathbf{L}^2$, L_z and the Hamiltonian describing the interaction, but L_{1z} and L_{2z} will not. Likewise, for an

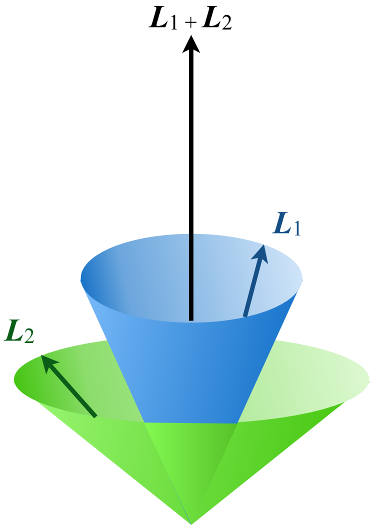


Fig. 6.1 The orbital angular momenta of two electrons, L_1 and L_2, are coupled trough electrostatic interaction. As a result, they will both process, whereas their sum is constant in time.

electron spin interacting with the same electron's orbital angular momentum, $\mathbf{L}_i$ and $\mathbf{S}_i$ will process around their sum $\mathbf{J}_i$, as described in chapter 4.

It is clear that sums of angular momenta play an important role, and thus we have to know with what restrictions such additions can be made. To start with: from classical physics it is clear that a sum of angular momenta is in itself an angular momentum. Moreover, we know that a general quantum mechanical angular momentum $\mathbf{J}$ must be quantized such that the eigenvalues of $\mathbf{J}^2$ are $j(j+1)$, with j being either zero, a positive integer, or a positive half-integer, and the eigenvalues of J_z are m_j, whose possible values lie between $-j$ and j and are separated by integer numbers (see appendix C).

With this, we can illustrate the addition rules with a few practical examples. A more rigorous justification for these rules is given in appendix I. We begin by considering a number of valence electrons with spins $\mathbf{S}_i$ that interact to form a total spin $\mathbf{S} = \sum_i \mathbf{S}_i$. We know that for every electron, $s_i = \frac{1}{2}$, and we assume that the orbital angular momenta (and/or the principal quantum numbers) are such that we do not have to bother with the Pauli principle. We write the quantum numbers associated with $\mathbf{S}^2$ and S_z as S and M_S respectively (see chapter 1.5), and the possible values of S are illustrated in figure 6.2.

For a case with two valence electrons, the possible results for the total spin are $S = 0$ or $S = 1$ — the two spins are either aligned or anti-parallel. These two options correspond to the singlets and triplets described in chapter 2.2. With a third electron, the third spin-vector must be added to the vector sum of the two first, either increasing or decreasing the total spin, and the possible values are $S = 1/2$ and $S = 3/2$. Those values gives spectral lines appearing in doublets and quartets, and we see that there is indeed a logical link between the total spin S, and the quantity $2S+1$, which was assumed to be the multiplicity (see chapter 1.5). It should be noted that some

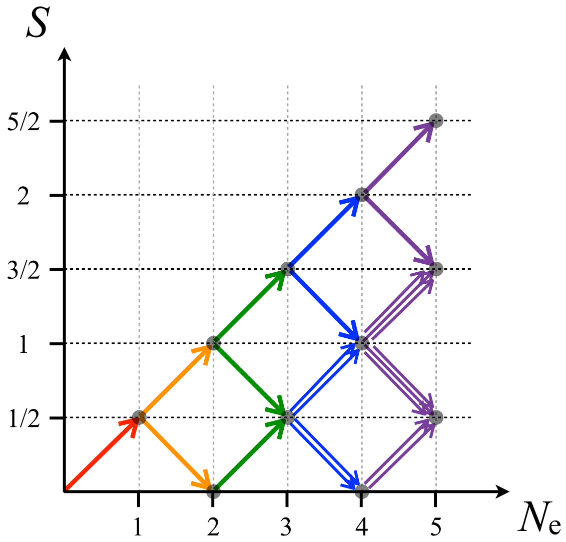


Fig. 6.2 Illustration of the vector addition of electron spins. On the x-axis is the number of electrons, and on the y-axis the total spin (the vector sum). With two electrons, only singlets ($S = 0$) and triplets ($S = 1$) are possible. Three electrons produces doublets ($S = 1/2$) and ($S = 3/2$) quartets, and so on. Note that is this diagram, it is assumed that the Pauli principle is not an impediment (some of the other quantum numbers are different).

of the addition paths in figure 6.2 may in some instances be inhibited by the Pauli principle.

Adding orbital angular momenta works in the same way, except that the different l_i can be any positive integer, but are never half-integers. Take an example with one d-electron ($l_1 = 2$) and one p-electron ($l_2 = 1$). The possible values of the quantum number for the total angular momentum, L, are 3, 2 and 1. If there is a third electron, its angular momentum is added in the same way to the different sums of the first two. At this stage, the order of the summation does not matter.

Left to do is to take into account the spin-orbit interaction. Here we are faced with a choice. We can either first couple all the individual $\mathbf{L}_i$ and $\mathbf{S}_i$ to a number of $\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i$, whereafter all the individual $\mathbf{J}_i$ are summed into a grand total angular momentum, $\mathbf{J} = \sum_i \mathbf{J}_i$. Alternatively, we first form $\mathbf{L} = \sum_i \mathbf{L}_i$ and $\mathbf{S} = \sum_i \mathbf{S}_i$, and after that we get to the same $\mathbf{J} = \mathbf{L} + \mathbf{S}$, having taken a different route. This is illustrated in figure 6.3

What path we take in order to get to $\mathbf{J}$ is actually crucial. Even when we exclude angular effects from inner, closed shells, we will have two angular momenta per valence electrons, and they will all interact each other. We have already resigned to calculate energy contributions with perturbation theory, using CFA electron configurations as zero-order states. However, if we take the Hamiltonian from (5.2) and (5.4), and add the spin-orbit contribution from (4.16):

$$H = H_{\mathrm{CF}} + H_{\mathrm{to}} + H_{\mathrm{SO}} , \tag{6.2}$$

we still need to treat the last two terms one by one. For a perturbative calculation, that will only work if the largest term is treated first, and if each subsequent term in the stepwise calculation has an energy contribution significantly smaller than the

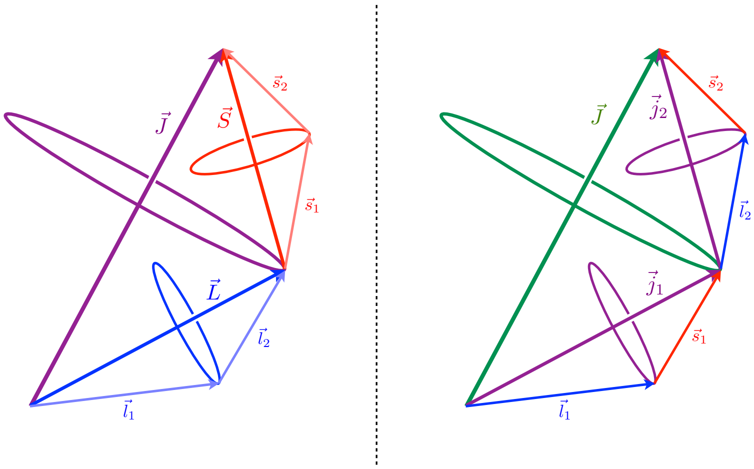


Fig. 6.3 Two different ways to couple the four angular momenta of a two electron atom ($\mathbf{L}_1$, $\mathbf{S}_1$,$\mathbf{L}_2$ and $\mathbf{S}_2$) in order to form the total electronic angular momentum **2**. In the left panel, the strongest interaction is that between the electrons. The individual $\mathbf{L}_i$ and $\mathbf{S}_i$ first couple to form **L** and **S**, and the the spin orbit interaction gives us **J**. This is the *LS*-coupling approximation. In the right panel, the spin-orbit interaction is the most pronounces. In this — the jj-coupling case — the individual $\mathbf{J}_i$ are first formed, and then these couple due to the electron-electron interaction and will give us **J**

preceding one. That is to say that both pictogram in figure 6.3 represents approximations and represent two limiting cases.

What this means is that we need to know the relative importance of H_{to} and H_{SO}, and the answer to that question is not universal. For light atoms, and for a considerable part of the periodic system, the interaction between electrons is much more important than the spin-orbit interaction. In that case, we first treat H_{to}, and the result are states referred to as atomic terms. For these, the first stage on the path to **J** has been to form **L** and **S** from the angular momenta of the individual electrons. The situation is referred to as '*LS*–coupling', and it will be treated in chapters 6.3 and 7. In the final step (ignoring external fields and nuclear effects), the term H_{SO} is applied as a perturbation to the atomic terms. This reveals the 'fine structure', which will be quantified in the quantum number J. The representation of the states in *LS*-coupling is:

$$|\gamma LSJM_J\rangle\ . \tag{6.3}$$

The fine-structure Hamiltonian H_{SO} scales as Z^3 — see (4.12) — whereas H_{to} has a linear scaling with Z. As a consequence the approximation that the spin-orbit term is small compared with the Coulomb torque one may not hold for very heavy atoms.

In the other extreme limit, we will have the case where we can safely inverse the order in which the two angular Hamiltonians are applied. In these cases, the internal spin–orbit interaction swamps the coupling between the valence electrons. This situations is what is illustrated in the right part of figure 6.3. We call this 'jj–coupling', since we begin by forming the individual $\mathbf{J}_i$, and then we add all these to form $\mathbf{J}$. The quantum numbers L and S no longer commutes with the total Hamiltonian, and the representation must rather be:

$$|\,\gamma j_1 \ldots j_N J M_J\,\rangle \, . \tag{6.4}$$

We treat jj–coupling in chapters 6.4 and 8.

Obviously both LS–coupling and jj-coupling are approximations. However, with these descriptions as a basis, we are able to describe also many intermediate cases. We will look closer at such cases in chapter 9.

6.3 *LS*-coupling

In the *LS*-coupling approximation, we assume that the angular part of the interaction *between* electrons is so much stronger than the spin-orbit interaction, intrinsic for each electron, that the latter can be ignored in a first step of the approximation. Once we have specified the electronic configuration, the next step is thus to form the quantum numbers L and S, and we will assume that the corresponding operators $\mathbf{L}^2$ and $\mathbf{S}^2$ commute with the Hamiltonian. More generally, we will take this as a definition of *LS*-coupling schemes, that is ones for which the Hamiltonian is diagonal in L and S.

We saw in chapter 6.2 that we can ignore electrons in closed shells. The process of adding up the different $\mathbf{L}_i$ and $\mathbf{S}_i$ for the valence electrons is done as covered in chapter 6.1 and as illustrated in figure xxxxxXXX.

The quantum numbers L can be zero or any positive integer. It is annotated in a way analogous to that on the orbital angular momentum of individual electrons (see chapter 1.5), but with capital letters. A total angular momentum of $L = 0$ will be annotated ‘S’, $L = 1$ ‘P’, $L = 2$ ‘D’ and so on. This letter symbol will be the basis of the *LS*-coupling term.

The total spin, S, will be half-integer for an odd number of electrons, and integer or zero for an even number. In an *LS*-coupling term, the value of S is indicated by writing the numerical value of $2S+1$ as a superscript to the right of the letter symbol for L. $2S+1$ is called the multiplicity of the term, for reasons that will be clarified in the following.

6.3.1 Atomic terms

We will look more closely at the total number of quantum numbers needed to describe an atomic state, and the multiplicity (or degeneracy) of a ${}^{2S+1}L$-term. For an individual electron, we need the four quantum numbers n, l, m_l and m_s to describe a state, which corresponds to nu numbers of degrees of freedom. For an N-electron atom, we can therefore assume that we have $4N$ degrees, and a need for 4N quantum numbers.

Suppose that the number of atoms in closed shells is N_c and the number of valence electrons is N_o, with $N_\mathrm{c} + N_\mathrm{o} = N$. Within the CFA, we describe the closed shells with their corresponding part of the electron configuration, which will gives us N_c pairs of n and l. In light of the Pauli principle — which is the effect making these shells ‘closed’ in the first place — this will actually specify all four relevant quantum numbers for these electrons. This leaves us with another $4N_\mathrm{o}$ to be determined.

The valence part of the configuration provides $2N_\mathrm{o}$ numbers. For the remaining $2N_\mathrm{o}$, thing will depend on how many valence electrons we have. If there is only one, only two degrees of freedom remains, and specifying the ”total quantum numbers based on L and S, that is either $|LSM_LM_S\rangle$ or $|LSLM_J\rangle$, gives apparently give us too many quantum numbers. This is not actually a problem, since in this case, we will always have $L = l$ and $S = s = 1/2$.

For two valence electrons, the sets $|LSJM_J\rangle$ or $|LSM_LM_S\rangle$ will do perfectly to provide a full description. If we have three or more valence electrons, the *LS*-coupling designation is incomplete. This latter situation diverges for cases where all electrons are in the same orbital or not. If they are not, a 'parent term' can be formed before the final atomic term is specified. If the valence electrons are indeed in identical n_i and l_i, the actual number of degrees of freedoms will be limited by the Pauli principle, and the *LS*-description will be sufficient after all.

In the *LS*-coupling approximation, we will thus specify an atomic term for an *N*-electron atom as:

$$(n_1 l_1 \dots n_{N_\mathrm{c}} l_{N_\mathrm{c}})\, n_{\mathrm{o}1} l_{\mathrm{o}1} \dots n_N l_N \; {}^{2S+1}L\,, \tag{6.18}$$

where the part of the electron configuration inside a parenthesis represents the valence electrons. This is more than often omitted in the representation. If parent terms are needed, the representation will be (with the valence configuration omitted for clarity):

$$n_{\mathrm{o}1} l_{\mathrm{o}1} \dots n_{N-1} l_{N-1} \left({}^{2S_\mathrm{p}+1}L_\mathrm{p}\right) n_N \; {}^{2S+1}L\,. \tag{6.19}$$

In a case with a many valence electrons (for example a d-orbital with four or more electrons), more than one parent term may be needed. The the atomic terms above will be added specification for the remaining quantum numbers, when more perturbations such as the spin-orbit coupling are added.

6.3.2 Two non-equivalent electrons

To give concrete examples, we start by showing the possible atomic terms for a case of two valence electrons that are *not* in the same orbitals. That is, we have either or both of the conditions $n_1 \neq n_2$ and $l_1 \neq l_2$ fulfilled (we now ignore the electrons if the inner shell and simply index the valance electrons beginning with one). This is the simplest case, since then we do not have to be careful about obeying the Pauli principle. We can never make these two electrons equivalent my specifying m_{l1}, m_{l2}, m_{s1} and m_{s2}. In the following, we will give to examples — the configurations 2p3p and 3d4p.

For the 2p3p-configuration (or any n_1pn_2p with $n_1 \neq n_2$), we have $l_1 = l_2 = 1$ and as always $s_1 = s_2 = 1/2$. The values for m_{l1} and m_{l2} can be +1, 0 or -1, and the spins can be parallel or anti-parallel with the chosen quantization axis ('up' or 'down'). With all possible permutations, this should give us 36 different states, where many may be degenerate in energy. When l_1 and l_2 couples, the possible values for L are 2, 1 or 0. The two electrons spins can be either mutually parallel or anti-parallel, giving the possible values of 1 or 0 for S. The possible terms for the configuration 2p3p are thus:

$${}^1\mathrm{D}\,,\,{}^3\mathrm{D}\,,\,{}^1\mathrm{P}\,,\,{}^3\mathrm{P}\,,\,{}^1\mathrm{S}\,,\,{}^3\mathrm{S}\,. \tag{6.20}$$

If we choose to specify the rest of the term with the quantum numbers J and J_M (which will prove to be appropriate in the absence of external fields), we can make an accounting of the number of state, and show that it is indeed 36. We know the for each term, the possible values for J are between $L+S$ and $|L-S|$. This is illustrated in table 6.1.

Table 6.1 Possible *LS*-coupling states for a 2p3p-configuration

term	J	M_J	number of states
^{1}D	2	$-2\ldots2$	5
^{3}D	3	$-3\ldots3$	7
	2	$-2\ldots2$	5
	1	$-1\ldots1$	3
^{1}P	1	$-1\ldots1$	3
^{3}P	2	$-2\ldots2$	5
	1	$-1\ldots1$	3
	0	0	1
^{1}S	0	0	1
^{3}S	1	$-1\ldots1$	3
Total number of states:			36

For the 3d4p-configuration, S is still 0 or 1, and L can vary between 3 and 1. The possible terms become:

$$^1\mathrm{F},\, ^3\mathrm{F},\, ^1\mathrm{D},\, ^3\mathrm{D},\, ^1\mathrm{P},\, ^3\mathrm{P}\,, \tag{6.21}$$

and if we count the number of possible state, we in this case get 60.

6.3.3 Two equivalent electrons

To exemplify this case, we take the configuration 2p^2 (the ground state configuration for atom number 6, C). Had it not been for the Pauli principle, the possible terms would have been the same as in the case for 2p3p, shown in (6.20). However, in this case our electrons are equivalent and we must take into account that only exchange anti-symmetric wave functions are possible. We must exclude atomic terms that are only possible for electrons equivalent. We must also exclude combinations of m_{l1}, m_{s1}, m_{l2} and m_{s2} that are the same for equivalent electrons.

A practical way to illustrate this is to use a table representation of the above individual electron quantum numbers, introduced by Condon & Shortley. Such a table is organised horizontally and vertically by the total angular momentum projection numbers $M_L = m_{l1} + m_{l2}$ and $M_S = m_{s1} + m_{s2}$. To illustrate this, we first show an example for the already treated configuration 2p3p in table 6.2. Each entry in this table is a pair of electrons, with the numerical values showing m_{li} and the plus/minus superscripts indicates m_{li}. We see that M_L can vary between 2 and -2, which means that the maximum value of L is to, and that $S = 1$ is the maximum total spin, since M_S is between 1 and -1. We also see that we have 36 states in total, which is fully consistent with what we showed in chapter 6.3.2.

Table 6.2 ghghhghgh

2p3p		M_S		
		1	0	-1
M_L	2	$(\ 1^+\ \ 1^+\ )$	$(\ 1^+\ \ 1^-\ )\,(\ 1^-\ \ 1^+\ )$	$(\ 1^-\ \ 1^-\ )$
	1	$(\ 1^+\ \ 0^+\ )$ $(\ 0^+\ \ 1^+\ )$	$(\ 1^+\ \ 0^-\ )\,(\ 1^-\ \ 0^+\ )$ $(\ 0^+\ \ 1^-\ )\,(\ 0^-\ \ 1^+\ )$	$(\ 1^-\ \ 0^-\ )$ $(\ 0^-\ \ 1^-\ )$
	0	$(\ 1^+\ -1^+\ )$ $(\ 0^+\ \ 0^+\ )$ $(\ -1^+\ \ 1^+\ )$	$(\ 1^+\ -1^-\ )\,(\ 1^-\ -1^+\ )$ $(\ 0^+\ \ 0^-\ )\,(\ 0^-\ \ 0^+\ )$ $(\ -1^+\ \ 1^-\ )\,(\ -1^-\ \ 1^+\ )$	$(\ 1^-\ -1^-\ )$ $(\ 0^-\ \ 0^-\ )$ $(\ -1^-\ \ 1^-\ )$
	-1	$(\ 0^+\ -1^+\ )$ $(\ -1^+\ \ 0^+\ )$	$(\ 0^+\ -1^-\ )\,(\ 0^-\ -1^+\ )$ $(\ -1^+\ \ 0^-\ )\,(\ -1^-\ \ 0^+\ )$	$(\ 0^-\ -1^-\ )$ $(\ -1^-\ \ 0^-\ )$
	-2	$(\ -1^+\ -1^+\ )$	$(\ -1^+\ -1^-\ )\,(\ -1^-\ -1^+\ )$	$(\ -1^-\ -1^-\ )$

For the case with the 2p3p-configuration, a table such as table 6.2 is superfluous. However, for the case with equivalent electrons it will help. Consider the same type of table for the $2p^2$-configuration. Initially, we can copy table 6.2, but then a number of terms have to be deleted. We have to remove pairs of identical electrons, such as $(1^+\ 1^+)$. Furthermore, with identical electrons we have some pairs that identical, such as $(1^+\ 1^-)$ and $(1^-\ 1^+)$; these also have to go. We end up with table 6.3. The 36 states have been reduced to 15. Some terms are no longer feasible. For example ^{3}D is no longer possible, since we cannot have $M_L = 2$ and $M_S = 1$ at the same time. We still need at least one triplet, and we can make out from table 6.3 that we must have a ^{3}P-term. If we contemplate the possible values of J and M_J for ^{3}P, we find that it corresponds to 9 states. We can then remove 9 electron pairs from table 6.3, with M_S- and M_L-values both between 1 and -1. For what remains in the table, we see that we must also have a term ^{1}D. This will take care of five states, which means that the only thing remaining in table 6.3 will be a lone electron pair for $M_L = 0$ and $M_S = 0$. This has to correspond to ^{1}S.

We conclude that the possible LS-coupling terms for the $2p^2$-configuration are:

Table 6.3 Diagram for identification of *LS*-coupling terms not in conflict with the Pauli principle, for the 2p^2-configuration.

2p^2		M_S		
		1	0	-1
M_L	2		$(\ 1^+\ \ 1^-\ )$	
	1	$(\ 1^+\ \ 0^+\ )$	$(\ 1^+\ \ 0^-\ )$ $(\ 0^+\ \ 1^-\ )$	$(\ 1^-\ \ 0^-\ )$
	0	$(\ 1^+\ -1^+\ )$	$(\ 1^+\ -1^-\ )$ $(\ 0^+\ \ 0^-\ )$ $(\ -1^+\ \ 1^-\ )$	$(\ 1^-\ -1^-\ )$
	-1	$(\ 0^+\ -1^+\ )$	$(\ 0^+\ -1^-\ )$ $(\ -1^+\ \ 0^-\ )$	$(\ 0^-\ -1^-\ )$
	-2		$(\ -1^+\ -1^-\ )$	

$$^1\mathrm{D}\,,\,^3\mathrm{P}\,,\,^1\mathrm{S}\,, \tag{6.22}$$

and in table 6.4 we show that we get 15 different states, as predicted.

Table 6.4 Possible *LS*-coupling states for a 2p^2-configuration

term	J	M_J	number of states
^{1}D	2	$-2\ldots 2$	5
^{3}P	2	$-2\ldots 2$	5
	1	$-1\ldots 1$	3
	0	0	1
^{1}S	0	0	1
Total number of states:			15

6.3.4 More than two valence electrons

Also with three or more valence electrons, it will make a big difference if all or some of the electrons are equivalent. The best way to show how *LS*-coupling terms can be identified is via examples.

Suppose we have three identical p-orbital electrons, such as the ground state configuration in N, $2p^3$. Making a diagram such as tables 6.2 or 6.3 may at first glance appear unattractive, due to the large number of combination. If the electrons had been inequivalent (such as the exotic doubly excited configuration 2p3p4p), we would have had 256 combinations of the different m_{li} and m_{si}, and thus a big and cumbersome table.

However, with identical electrons, a vast majority of these trios of quantum numbers must be excluded. Moreover, the symmetry of a diagram like table 6.3 means that suffices to construct one quadrant of, while including the $M_L = 0$ row and the possible $M_S = 0$ column. For the $2p^3$ example, we get a diagram as in table 6.5. From this, we can extract that the only possible terms are:

Table 6.5 ghghhghgh

$2p^3$		M_S	
		3/2	1/2
M_L	3		
	2		(1^+ 1^- 0^+)
	1		(1^+ 1^- -1^+) (1^+ 0^+ 0^-)
	0	(0^+ -1^+ -1^+)	(1^+ 0^+ -1^-) (1^+ 0^- -1^+) (1^- 0^+ -1^+)

$$^2\mathrm{D}\,,\,^2\mathrm{P}\,,\,^4\mathrm{S}\,, \tag{6.23}$$

If we instead study an excited configuration of N, such as $2p^2 3s$, we have to first couple two of the electrons, and then add the third, at every step taking into account the Pauli principle as necessary. The final result is the same no matter which electron pair one starts with, but the most logic procedure, and the standardised one, is to being with the most tightly bound electrons, and then successively add the more loosely bound.

For $2p^2 3s$, we form the parent terms from the two equivalent 2p electrons, which we found in (6.22). To these three parent terms, we add the 3s-electron, with $l_3 = 0$ and $s_3 = 1/2$, with all possible projections of m_{l3} and m_{s3}. We find four possible *LS*-coupling terms:

$$\begin{aligned}&2p^2(^1D)\,3s\,^2D\\&2p^2(^3P)\,3s\,^4P\\&2p^2(^3P)\,3s\,^2P\\&2p^2(^1S)\,3s\,^2S\,.\end{aligned}\tag{6.24}$$

6.3.5 Fine structure

We will finish this introduction to the *LS*-coupling scheme by adding the spin-orbit Hamiltonian of 4.16. To recapitulate; we have first applied the CFA in order to get a separable Schrödinger equation and an electron configuration zero-order state. We have then applied what is left of the electron-electron repulsion, the Coulomb torque Hamiltonian of 5.4, as a perturbation. That has split and/or shifted the configuration states into *LS*-coupling terms, with a degeneracy in energy of $(2L+1)(2S+1)$. We will now remove a part of that degeneracy by applying the spin-orbit interaction as yet another Hamiltonian.

We begin by slightly reformulating 4.16:

$$H_{\mathrm{SO}} = \sum_i^N f(r_i)\,\mathbf{L}_i\cdot\mathbf{S}_i = \left[\sum_i^N \xi(r_i)\right]\,\mathbf{L}\cdot\mathbf{S}\,. \tag{6.25}$$

We now restrict the summation to the valence electrons (based on the arguments given in chapter 6.2), and we have taken the *LS*-coupling approximation that the individual spins and orbital angular momenta couple to **S** and **L** so strongly that other interaction only perturb this coupling marginally.

The Hamiltonian given in the last line of (6.25) commutes with **J**. This means that is will be diagonal in J and M_J, and this can also be seen as the essence of the *LS*-coupling approximation. Non-diagonal terms in J would signal the departure from the *LS*-coupling, and would make the last equality in (6.25) invalid. It should, however, be noted that by its very nature, the spin-orbit Hamiltonian does not commute with **L** and **S**. M_L and M_S will not provide good quantum numbers, but within the approximation that $\mathbf{L^2}$ and $\mathbf{S}^2$ do commute with (6.25), the diagonal representation is:

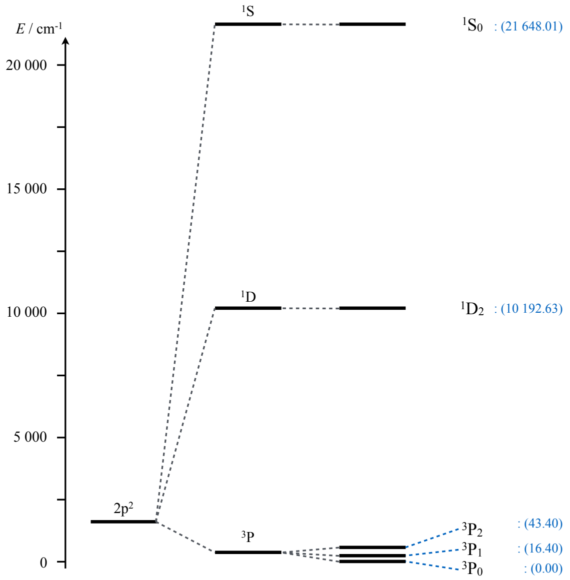
$$|LSJM_J\rangle\,. \tag{6.26}$$

The energy correction to to the perturbation (6.25) will be:

$$E_{\mathrm{SO}} = \left\langle\left[\sum_i^N \xi(r_i)\right]\right\rangle\langle\mathbf{L}\cdot\mathbf{S}\rangle\,. \tag{6.27}$$

The first factor in (6.27) can only be calculated analytically if we know the wave function, which we do not. It can however, be derived empirically from spectroscopical data, and it can also be estimated by approximative and/or numerical methods

Fig. 6.4 ghghghhghghg



(see chapters 7 and 14). We define the 'fine structure factor' for a certain term thus:

$$A(\gamma LS) \equiv \left\langle \gamma LS \left| \left[\sum_i^N \xi(r_i) \right] \right| \gamma LS \right\rangle . \tag{6.28}$$

Here, γ is as usual short for the electron configuration. We see that the fine structure factor depends on L and S, making it specific for each atomic term, but that it is independent of J.

The second factor of (6.27) can be calculates as was done in 4.9. That is, we have:

$$E_{\mathrm{SO}} = \frac{A(\gamma LS)}{2} \left[J(J+1) - L(L+1) - S(S+1) \right] . \tag{6.29}$$

This means that every LS-term will be split up in $(2S+1)$ 'fine-structure levels' (or $2L+1$ if $S > L$). This will be annotated by adding the quantum number J to the LS-coupling term:

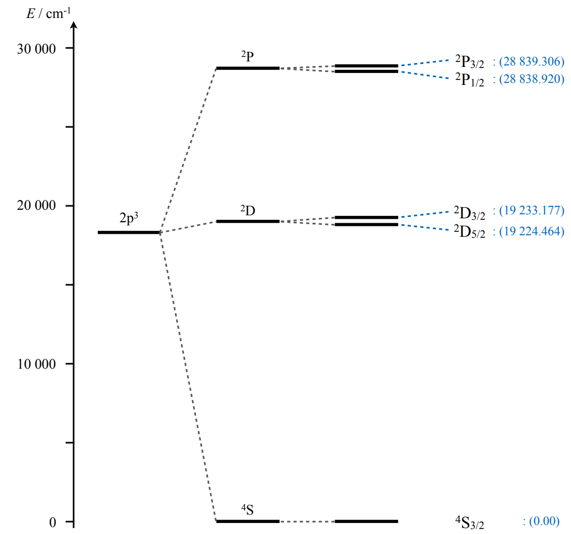
$$^{2S+1}L_J . \tag{6.30}$$

The $(2J+1)$-fold degeneracy in M_J will remain.

In figures 6.4 and 6.5, we illustrate in partial energy level diagrams how this can play out. These examples are for the $2p^2$ and $2p^3$ configurations respectively, where the terms were found in (6.22) and (6.23). The energy values given are experimental values for neutral C ($2p^2$) and N ($2p^3$) respectively.

For the doublet $^2D_{5/2}$ and $^2D_{3/2}$ in figure 6.5, we see that the fine structure factor can be negative. The small splittings in the multiplets compared to the energy

Fig. 6.5 ghghghhghghg



difference between the term shows that *LS*-coupling is a good approximation in this case.We will defer a discussion on the energy order of the terms until chapter 7.

For every term with a multiplicity of two or larger, the fine structure factor $\zeta(\gamma LS)$ can be deduced from experimental data and (6.29). In figure 6.4, we see that the interval between $^3P_2$ and $^3P_1$ is close to twice as great as that between $^3P_1$ and $^3P_0$. This is roughly consistent with (6.29).

We can take a closer look at the energy interval between fine-structure levels in *LS*-coupling. From (6.29), we can calculate this interval as:

$$E_{\mathrm{SO}}(\gamma,L,S,J) - E_{\mathrm{SO}}(\gamma,L,S,J-1) = A(\gamma LS)\,J\ . \tag{6.31}$$

This is known as 'Landé's interval rule', which shows that the interval between two adjacent levels is directly proportional to the one of them with the highest *J*. It is useful in empirical analyses of spectra, and it can be used as a measure of the goodness of the *LS*-coupling approximation.

6.4 *jj*-coupling

The *LS*-coupling described in the preceding chapter is a limiting case, and at the other extreme end of this scale we have *jj*-coupling. This occurs when the energy contribution of H_{SO} in (6.2) is so large that H_{to} can at first be neglected. As we have seen, the Coulomb torque Hamiltonian scales linearly with the atomic number, while the spin-orbit Hamiltonian is proportional to its fourth power.

In terms of the vector model, this means that we first have to couple the $\mathbf{L}_i$ and $\mathbf{S}_i$ of each individual valence electron (we can still take the average effect of all closed shells as spherically symmetric). That is, we form the quantum numbers j_i and m_{ji} from all the l_i, m_{li}, s_i and m_{si}, following the rules for quantum mechanical vector addition, outlined in chapter 6.1. For the case of two valence electrons, this is what is illustrated in the right panel on figure 6.3. The quantum numbers m_{li} and m_{si} will no longer be 'good', since their corresponding angular momentum projections are not constants of motion under the interaction.

The Hamiltonian that will be used in jj-coupling is:

$$H = H_{\mathrm{CF}} + H_{\mathrm{SO}} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i V_{\mathrm{CF}_i}(r_i) + \sum_i \xi(r_i)\,\mathbf{L}_i \cdot \mathbf{S}_i\,, \tag{6.32}$$

The first two terms will give the zero-order solutions, which also here are the electronic configuration. The CFA is still applied in the same way. The solutions will be degenerate in m_{li} and m_{si}, and after forming Slater determinant combinations of these, the spin-orbit Hamiltonian can be applied as a perturbation.

An important difference between (6.4) and the Hamiltonian used in *LS*-coupling is the absence of cross-couplings between the electrons. Equation (6.4) is a sum of single-electron Hamiltonians, and we can designate the solutions as:

$$(n_1, l_1, j_1, \ldots, n_N, l_N, j_N)\,, \tag{6.33}$$

where N is used for the number of electrons outside closed orbitals. Such sets will be the jj-coupling terms. The fine structure in jj-coupling will appear when the Hamiltonian H_{to} is applied as a subsequent perturbation. In the vector image, the $\mathbf{J}_i$ will combine to a $\mathbf{J}$, and we will get fine structure levels described by quantum numbers J.

We have seen that *LS*-coupling is a good approximation for light atoms. In contrast, jj-coupling rarely appears in pure form. Even for very heavy atoms, we often see a mixed case. Some of these will be presented in chapter 9.

One set of elements that display almost pure jj-coupling is highly charged heavy ions. In these, the strong binding energy of the valence electron will diminish the relative importance of the Coulomb exchange term. Even for elements and atomic states that are neither *LS*-coupled, nor jj-coupled, an understanding of the two limiting case will facilitate the understanding of the atomic structure.

6.4.1 jj-coupling terms

The terms in jj-coupling will be made up of the ensemble of all the j_i among the valence electrons. Even though the electrons do not interact at this level of interaction, there will still some combinations of quantum numbers that will be prohibited by the Pauli principle, and the procedure to follow in order to identify these will resemble that used for *LS*-coupling.

The notation for jj-coupling has not become as standardised as is the case for *LS*-coupling. The one we will use in this book is where the electrons in open shells are divided into groups with common values of n_i, l_i and j_i. The electron configuration of closed shells is notated in the same way as for *LS*-coupling. Examples of how the valence electrons can be annotated are as follows:

$$\begin{aligned} &[6\mathrm{p}^2_{1/2}] \\ &[5\mathrm{d}^2_{5/2}\, 5\mathrm{d}_{3/2}]\,. \end{aligned} \tag{6.34}$$

In the first example, there are two electrons, with $n_1 = n_2 = 6$, $l_1 = l_2 = 1$, and $j_1 = j_2 = 1/2$. Note that this combination does not violate the Pauli principle. We could have $m_{l1} = 1, m_{s1} = -1/2, m_{j1} = 1/2$; and $m_{l2} = -1, m_{s2} = 1/2, m_{j2} = -1/2$. In the second example, we have three 5d-electrons. Two of them have $j_1 = j_2 = 5/2$, and the third has $j_3 = 3/2$.

For non-equivalent electrons, identifying the possible *jj*-coupling terms is an easy task. As an example, we take the configuration 6p7p. The possible terms will be:

$$[6\mathrm{p}_{3/2}\, 7\mathrm{p}_{3/2}]\,,\, [6\mathrm{p}_{3/2}\, 7\mathrm{p}_{1/2}]\,,\, [6\mathrm{p}_{1/2}\, 7\mathrm{p}_{3/2}]\,,\, [6\mathrm{p}_{1/2}\, 7\mathrm{p}_{1/2}]\,. \tag{6.35}$$

For the sake of comparison with the *LS*-couples 2p3p-configuration shown in table 6.1, we can tabulate the terms in (6.35), with the respective possible *J*-values, and keep a record of the possible number of states. This is done in table 6.6. We find that the number of states is consistent with what it was when we coupled two non-equivalent p-electrons with *LS*-coupling.

Table 6.6 Possible *jj*-coupling states for a 6p7p-configuration

term	J	M_J	number of states
$[6\mathrm{p}_{3/2}\, 7\mathrm{p}_{3/2}]$	3	$-3\ldots3$	7
	2	$-2\ldots2$	5
	1	$-1\ldots1$	3
	0	0	1
$[6\mathrm{p}_{3/2}\, 7\mathrm{p}_{1/2}]$	2	$-2\ldots2$	5
	1	$-1\ldots1$	3
$[6\mathrm{p}_{1/2}\, 7\mathrm{p}_{3/2}]$	2	$-2\ldots2$	5
	1	$-1\ldots1$	3
$[6\mathrm{p}_{1/2}\, 7\mathrm{p}_{1/2}]$	1	$-1\ldots1$	3
	0	0	1
Total number of states:			36

6.4.2 Equivalent electrons

An example of two equivalent electrons, where jj-coupling plays an important role is the ground configuration of lead: 6p^2. Even in this case, the jj-coupling is not quite pure, but we will use this as an example nevertheless. We know from table 6.6 that had the electrons been non-equivalent, we would have had M_J-values between 3 and -3, and we would have had 36 states altogether. In order to figure out which states that are not forbidden by the Pauli principle, we can make a diagram similar to those used in chapter 6.3.3. This is shown in table 6.7, where the entries in the table are pairs of the quantum numbers m_{j1} och m_{j2}. In agreement with the case for the 2p^2-configuration in table 6.3, we get 15 possible states.

Table 6.7 Diagram for identification of jj-coupling terms not in conflict with the Pauli principle, for the 6p^2-configuration.

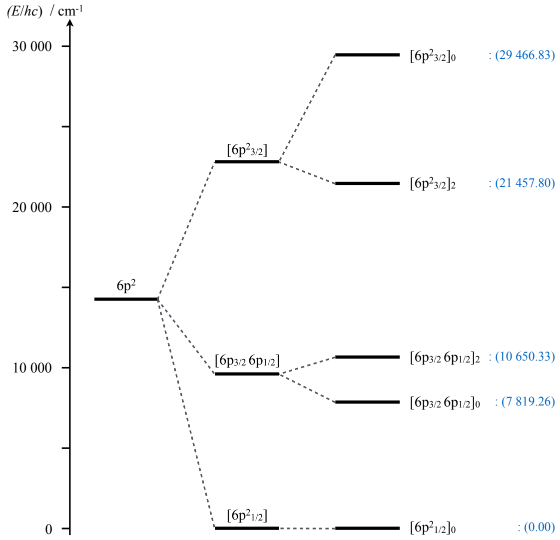
6p^2		j_1 j_2		
		3/2 3/2	3/2 1/2	1/2 1/2
M_J	3			
	2	(3/2 1/2)	(3/2 1/2)	
	1	(3/2 -1/2)	(3/2 -1/2) (1/2 1/2)	
	0	(3/2 -3/2) (1/2 -1/2)	(1/2 -1/2) (-1/2 1/2)	(1/2 -1/2)
	-1	(-1/2 3/2)	(-1/2 -1/2) (-3/2 1/2)	
	-2	(-3/2 -1/2)	(-3/2 -1/2)	
	-3			
possible J		2 , 0	2 , 1	0

A conclusion from table 6.7 is that the allowed jj-terms for the 6p^2-configuration are:

$$[6\mathrm{p}^2_{3/2}]_2\ ,\ [6\mathrm{p}^2_{3/2}]_0\ ,\ [6\mathrm{p}_{3/2}\,6\mathrm{p}_{1/2}]_2\ ,\ [6\mathrm{p}_{3/2}\,6\mathrm{p}_{1/2}]_1\ ,\ [6\mathrm{p}^2_{1/2}]_0\ . \tag{6.36}$$

In (6.36), we have also added the values of J (the jj-coupling fine structure) as a subscript to the terms. In chapter 8 we will give more a more complete account of which configurations that can lead to which jj-coupling terms.

Fig. 6.6 ghghghhghghg



6.4.3 Fine structure in jj-coupling

In order to make the jj-coupling complete, we must finally add the last term of the Hamiltonian in (6.2). This time, the last component to be added as a perturbation is the Coulomb torque Hamiltonian — the electron-electron repulsion.

The Hamiltonian H_{to} commutes with $\mathbf{J}^2$ and J_z, which means that a good diagonal representation will now be:

$$|n_1 l_1 j_1 \dots n_N l_n j_N J M_J\rangle \tag{6.37}$$

This time, the electrostatic mutual repulsion couples the different $\mathbf{J}_i$, which has the effect that the individual m_{ji} will no longer be good quantum numbers. Filled orbitals will have a total angular momentum of zero, as before.

To form the quantum number J, one has to follow the standard rules for addition of quantum mechanical angular momenta, outlined in chapter 6.1. If we again take the example of a jj-coupled p^2-configuration, as illustrated in table 6.7.

For two non-identical p-electrons, both the individual j_i can be either 3/2 or 1/2. This gives three different combinations. For $j_1 = j_2 = 3/2$, J can be 3, 2, 1 or 0. For $j_1 = 3/2$, $j_2 = 1/2$ (or inversely), the possible values are 2 and 1. For the last combination, $j_1 = j_2 = 3/2$, we have to have either $J = 1$ or $J = 0$. When the electrons are identical, we saw in the analysis accompanying table 6.7 that some of these combinations will be excluded, and we end up with the terms shown in (6.36).

In figure 6.6, we show the lowest energy states in Pb, which has the ground state configuration 6p^2. It should be noted that the jj-coupling is not pure in the ground state of Pb. The energy levels to the right of the figure are the experimentally measured energy levels. The two intermediate stages are here just statistical averages. In a *LS*-coupling scheme (see figure 6.4), the three lowest states would belong to the term ^{3}P, and the two upper ones would have been ^{1}D and ^{1}S. In many treaties of the lead atom, these levels are annotated with the *LS*-coupling notation, simply because that label is easier and more well known.

If the jj-coupling had been purer in lead, the three groups of levels in figure 6.6 would have been more distinct, and the within each term, the fine-structure splitting would have been smaller.

In chapter 8, we will look into this coupling scheme in more detail. We will study more complex electronic configurations — with more than two electrons — and we will add quantitative analyses.

Chapter 7
LS–coupling

The *LS*-coupling scheme was introduced in chapter 6 as a limiting example of the central field approximation. Each individual electron has both orbital angular momentum and a spin, and when we have two electrons or more, we will in total have at least four different angular moment that all interacts with each other via electromagnetic couplings. This means that the full wave function of the system will always be an entangled state.

When we try to disentangle this complication by first applying the CFA, and then treating the interactions between angular momenta in decreasing order of magnitude, we get different limiting cases. *LS*-coupling is the one where we assume that we first can apply only the angular contribution of the electrostatic interaction *between* the electrons as a perturbation, and only after that the spin-orbit interactions.

In this chapter, we will do several things. We will expand the initial treatment, introduced in chapter 6.3, to more complex situations, we will put the theory on a more rigorous theoretical footing,and we will go into much more detail. Initially, we will focus on *LS*-coupling atomic terms. After that, we will look at fine structure, and eventually we will explore the functional form of the *LS*-coupling states.

7.1 Atomic terms

The *LS*-coupling atomic terms are what we get when we apply the first perturbation term, the Coulomb torque Hamiltonian, to the electronic configuration. The latter will provide the zero-order states, and as we have seen in previous chapters, they have the great advantage that they give wave functions that are separable in individual electron coordinates.

Even though an electron configuration is an assignment of N hydrogenlike orbitals to N electrons, it does not make any sense to say that each individual electron *is* in one specified orbital. The crossterm means that the complete state will always be an entangled one, and that will be even more obvious when we apply degenerate perturbation theory — and are forced to use superposition states as the zero-order states in the calculation.

The Coulomb torque Hamiltonian (5.4) commutes with all the angular momentum operators of the entire atom, $\mathbf{L}^2$, L_z, $\mathbf{S}^2$, S_z, $\mathbf{J}^2$, and J_z. If (or rather when) we start take into account the spin orbit interaction, (4.16), the total Hamiltonian will no longer commute with L_z and S_z. Presently however, with H_{SO} neglected, there is no torque between $\mathbf{L}$ and $\mathbf{S}$, and hence the perturbation Hamiltonian that we use to produce the atomic terms, H_{to}, will not have any non-diagonal elements in M_L or M_S.

7.1.1 Allowed *LS*-coupling terms

We recall the notation for atomic terms, introduced in chapter 1.5, and used in chapter 6.3. The perturbation H_{to} will break the degeneracy in the quantum numbers L and S, which means that these two numbers will be enough to assign a term. The number L is for historic reasons annotated with a letter — S, P, D, F, … for $L = 0$, 1, 2, 3, …. To indicate S, one writes the *multiplicity* — $2S + 1$ — as a superscript to the right of the letter indicating L.

Added to that, atomic data tables often indicate whether a term has odd or even parity. An odd term gets a lowercase ‘o’ as a superscript to the right of the L-letter. For example, the ground state terms in C is the even term $2\mathrm{p}^2\ {}^3\mathrm{P}$, whereas an excited state is the odd term $2\mathrm{p}3\mathrm{s}\ {}^3\mathrm{P}^{\mathrm{o}}$.

Using diagrams like the examples in tables 6.2, 6.3 and 6.5, we can deduce the possible atomic terms for every conceivable electron configuration. If all electrons are non-equivalent, the task is easy. When they are equivalent, and we have to cater for the Pauli principle, it is slightly more challenging. It is also often more relevant, since most ground state configurations will have exclusively equivalent electrons.

We saw in tables 6.3 and 6.5 that is gets more complicated to find the allowed term for more valence electrons. This problem is alleviated due to a symmetry consideration. Consider N_{v} equivalent valence electrons in an orbital that can accommodate mximum N_{o} before it is full. The possible terms for $N_0 - N_{\mathrm{v}}$ valence electrons will be exactly the same as for N_{v} electrons. For example, a p^2-configuration will have the same terms as a p^6 one, a d^7-configuration will yield an identical group of terms as d^3, and so on.

This can be found by constructing charts like tables 6.3 and 6.5, but instead of entering the m_l- and m_s-values of the occupied orbitals, one does that for the unoccupied ones instead. The only difference in the table is that positive values of m_l- and m_s will then correspond to negative values of M_L- and M_S, but that does not change the conclusion.

In table 7.1, we give a table with the allowed *LS*-coupling terms for s- p- and d-configurations. Separately, in table 7.2, we show f-configurations. We point out yet again that only the valence electrons have to be included in this analysis, since all closed shell will only contribute with a ${}^1\mathrm{S}$ contribution (see chapter 6.2). As

Table 7.1 ghghhghgh

electron configuration			allowed terms			
s		^{2}S				
s^2	^{1}S					
p , p^5		^{2}P$^{\mathrm{o}}$				
p^2 , p^4	^{1}S , ^{1}D		^{3}P			
p^3		^{2}P$^{\mathrm{o}}$, ^{2}D$^{\mathrm{o}}$		^{4}S$^{\mathrm{o}}$		
d , d^9		^{2}D				
d^2 , d^8	^{1}S , ^{1}D ^{1}G		^{3}P , ^{3}F			
d^3 , d^7		^{2}P , ^{2}D$_{(2)}$ ^{2}F , ^{2}G ^{2}H		^{4}P , ^{4}F		
d^4 , d^6	^{1}S$_{(2)}$, ^{1}D$_{(2)}$ ^{1}F , ^{1}G$_{(2)}$ ^{1}I		^{3}P , ^{3}D ^{3}F$_{(2)}$, ^{3}G ^{3}H		^{5}D	
d^5		^{2}S , ^{2}P ^{2}D$_{(3)}$, ^{2}F$_{(2)}$ ^{2}G$_{(2)}$, ^{2}H ^{2}I		^{4}P , ^{4}D ^{4}F , ^{4}G		^{6}S

far as energy is concerned, the contribution from filled inner shells will change the energy, but only with an additive quantity that will be the same for all terms in the configuration. It will not affect the complexity of the structure.

Rather few of the terms in tables 7.1 and 7.2 will occur for atoms without considerable perturbations. To start with, the *LS*-coupling approximation will fail when the spin-orbit term of the total Hamiltonian gains importance, which will increasingly be the case as we go to heavier atoms. For example, this will affect essentially all atoms with 4f- and 5f-configuration ground states — the lanthanides and the actinides. Moreover, there will be many cases where different configurations are almost degenerate, which will in a strict sense invalidate the CFA. Notwithstanding, it will still be useful in most cases to identify terms in the *LS*-coupling scheme, and to then describe real observed energy levels as superpositions of these.

In tables 7.1 and 7.2, the numbers in brackets after some terms indicate that the term appears more than once for the configuration concerned. This can only occur for case with at least three valence electrons. In those cases, the quantum numbers L, S, M_L, and M_S are not sufficient for uniquely cover all the permutations of m_{li} and m_{si}

Table 7.2 ghghhghgh

electron configuration			allowed terms					
f , f^{13}		$^{2}F^{o}$						
f^{2} , f^{12}	^{1}S , ^{1}D ^{1}G , ^{1}I		^{3}P , ^{3}F ^{3}H					
f^{3} , f^{11}		$^{2}P^{o}$, $^{2}D^{o}_{(2)}$ $^{2}F^{o}_{(2)}$, $^{2}G^{o}_{(2)}$ $^{2}H^{o}_{(2)}$, $^{2}I^{o}$ $^{2}K^{o}$, $^{2}L^{o}$		$^{4}S^{o}$, $^{4}D^{o}$ $^{4}F^{o}$, $^{4}G^{o}$ $^{4}I^{o}$				
f^{4} , f^{10}	$^{1}S_{(2)}$, $^{1}D_{(4)}$ ^{1}F , $^{1}G_{(4)}$ $^{1}H_{(2)}$, $^{1}I_{(3)}$ ^{1}K, $^{1}L_{(2)}$ ^{1}N		$^{3}P_{(3)}$, $^{3}D_{(2)}$ $^{3}F_{(4)}$, $^{3}G_{(3)}$ $^{3}H_{(4)}$, $^{3}I_{(2)}$ $^{3}K_{(2)}$, ^{3}L ^{3}M		^{5}S , ^{5}D ^{5}F , ^{5}G ^{5}I			
f^{5} , f^{9}		$^{2}P^{o}_{(4)}$, $^{2}D^{o}_{(5)}$ $^{2}F^{o}_{(7)}$, $^{2}G^{o}_{(6)}$ $^{2}H^{o}_{(7)}$, $^{2}I^{o}_{(5)}$ $^{2}K^{o}_{(5)}$, $^{2}L^{o}_{(3)}$ $^{2}M^{o}_{(2)}$, $^{2}N^{o}$ $^{2}O^{o}$		$^{4}S^{o}$, $^{4}P^{o}_{(2)}$ $^{4}D^{o}_{(3)}$, $^{4}F^{o}_{(4)}$ $^{4}G^{o}_{(4)}$, $^{4}H^{o}_{(3)}$ $^{4}I^{o}_{(3)}$, $^{4}K^{o}_{(2)}$ $^{4}L^{o}$, $^{4}M^{o}$		$^{6}P^{o}$, $^{6}F^{o}$ $^{6}H^{o}$		
f^{6} , f^{8}	$^{1}S_{(4)}$, ^{1}P $^{1}D_{(6)}$, $^{1}F_{(4)}$ $^{1}G_{(8)}$, $^{1}H_{(4)}$ $^{1}I_{(7)}$, $^{1}K_{(3)}$ $^{1}L_{(4)}$, $^{1}M_{(2)}$ $^{1}N_{(2)}$, ^{1}Q		$^{3}P_{(6)}$, $^{3}D_{(5)}$ $^{3}F_{(9)}$, $^{3}G_{(7)}$ $^{3}H_{(9)}$, $^{3}I_{(6)}$ $^{3}K_{(6)}$, $^{3}L_{(3)}$ $^{3}M_{(3)}$, ^{3}N ^{3}O		^{5}S , ^{5}P $^{5}D_{(3)}$, $^{5}F_{(2)}$ $^{5}G_{(3)}$, $^{5}H_{(2)}$ $^{5}I_{(2)}$, ^{5}K ^{5}L		^{7}F	
f^{7}		$^{2}S^{o}_{(2)}$, $^{2}P^{o}_{(5)}$ $^{2}D^{o}_{(7)}$, $^{2}F^{o}_{(10)}$ $^{2}G^{o}_{(10)}$, $^{2}H^{o}_{(9)}$ $^{2}I^{o}_{(9)}$, $^{2}K^{o}_{(7)}$ $^{2}L^{o}_{(5)}$, $^{2}M^{o}_{(4)}$ $^{2}N^{o}_{(2)}$, $^{2}O^{o}$ $^{2}Q^{o}$		$^{4}S^{o}_{(2)}$, $^{4}P^{o}_{(2)}$ $^{4}D^{o}_{(6)}$, $^{4}F^{o}_{(5)}$ $^{4}G^{o}_{(7)}$, $^{4}H^{o}_{(5)}$ $^{4}I^{o}_{(5)}$, $^{4}K^{o}_{(3)}$ $^{4}L^{o}_{(3)}$, $^{4}M^{o}$ $^{4}N^{o}$		$^{6}P^{o}$, $^{6}D^{o}$ $^{6}F^{o}$, $^{6}G^{o}$ $^{6}H^{o}$, $^{6}I^{o}$		$^{8}S^{o}$

Table 7.3 ghghhghgh

d^3		M_S	
		3/2	1/2
	6		
	5		$(2^+\ 2^-\ 1^+)$
	4		$(2^+\ 2^-\ 0^+)\ (2^+\ 1^+\ 1^-)$
	3	$(2^+\ 1^+\ 0^+)$	$(2^+\ 2^-\ {-1}^+)\ (2^+\ 1^+\ 0^-)$ $(2^+\ 1^-\ 0^+)\ (2^-\ 1^+\ 0^+)$
M_L	2	$(2^+\ 1^+\ {-1}^+)$	$(2^+\ 2^-\ {-2}^+)\ (2^+\ 1^+\ {-1}^-)$ $(2^+\ 1^-\ {-1}^+)\ (2^-\ 1^+\ {-1}^+)$ $(2^+\ 0^+\ 0^-)\ (1^+\ 1^-\ 0^+)$
	1	$(2^+\ 1^+\ {-2}^+)$ $(2^+\ 0^+\ {-1}^+)$	$(2^+\ 1^+\ {-2}^-)\ (2^+\ 1^-\ {-2}^+)$ $(2^-\ 1^+\ {-2}^+)\ (2^+\ 0^+\ {-1}^-)$ $(2^+\ 0^-\ {-1}^+)\ (2^-\ 0^+\ {-1}^+)$ $(1^+\ 1^-\ {-1}^+)\ (1^+\ 0^+\ 0^-)$
	0	$(2^+\ 0^+\ {-2}^+)$ $(1^+\ 0^+\ {-1}^+)$	$(2^+\ 0^+\ {-2}^-)\ (2^+\ 0^-\ {-2}^+)$ $(2^-\ 0^+\ {-2}^+)\ (2^+\ {-1}^+\ {-1}^-)$ $(1^+\ 1^-\ {-2}^+)\ (1^+\ 0^+\ {-1}^-)$ $(1^+\ 0^-\ {-1}^+)\ (1^-\ 0^+\ {-1}^+)$

As an example, we give the term chart for a d^3-configuration in table 7.3. If we pick out the terms from this, with the procedure described in chapter 6.3, the first term we identify is ^{2}H. When we proceed, we get ^{2}G, ^{4}F and ^{2}F, but then we find that we have to use ^{2}D twice in order to account for all entries in the table. Finally, we get single occurrences of ^{4}P and ^{2}P, in accordance with table 7.1.

7.1.2 Genealogy of atomic terms

When a term occurs more than once for an electron configuration, the level can be more specified if it is possible to discriminate between different paths to the final vector coupling term. As an example, we can consider three non-equivalent electrons with the l-quantum numbers 0,1 and 2.

An analysis of the what possible terms that emanates from this spd-configuration yields the result: ^{4}F, $^2\mathrm{F}_{(2)}$, ^{4}D, $^2\mathrm{D}_{(2)}$, ^{4}P, $^2\mathrm{P}_{(2)}$. That is, all three doublets occur twice. In this case, we can differentiate between the terms that have the same notation.

If we first add the s- and p-electron, this gives the two possible terms ^{3}P and ^{1}P. If we now add the d-electron, we find the following possible terms for the spd-configuration (these terms are all of odd parity, but here we omit the superscript):

$$\begin{aligned} &\mathrm{sp}(^3\mathrm{P})\mathrm{d} \Rightarrow {}^4\mathrm{F},{}^2\mathrm{F},{}^4\mathrm{D},{}^2\mathrm{D},{}^4\mathrm{P},{}^2\mathrm{P} \\ &\mathrm{sp}(^1\mathrm{P})\mathrm{d} \Rightarrow {}^2\mathrm{F},{}^2\mathrm{D},{}^2\mathrm{P}\,. \end{aligned} \tag{7.1}$$

The terms in the brackets after sp are called parent terms. In most cases, the terms with the same final term, but with different parents, will have differing energies, and the way the quantum numbers have been specified in (7.1) is the representation that diagonalises the Hamiltonian.

We could also have begun by adding the s- and d-electron. That had resulted in the parent terms (^{3}D) and (^{1}D), and then of course the same set of final terms. The logical order to chose in which order to add the electron angular momentum vectors is to begin with the most tightly bound electrons. In that case, the final electron is in a manner of speaking added to an ionic term that is further specified by a parent term.

In the example in table 7.3 — with a d^3-configuration — it is not possible to specify parentage in this way. The three electrons are identical, and we have now way to discriminate between the two ^{2}D-terms.

A pure d^3-configuration is actually rare. Looking at the periodic system in figure 5.2, and the ground state configurations in table 5.1, it appears as if vanadium might have this configuration in its ground state. However, the tabulated configuration is 3d^{3}4s^2, which is because the 3d- and 4s-electrons have very similar binding energy. It is therefore more proper to treat V as an electron with five valence electrons, even if in the lowest energy state two of the five electrons fill up an s-orbital. Indeed, the lowest energy *LS*-coupling term of the excited configuration 3d^{4}4s will lie lower that most terms in 3d^{3}4s^2. To illustrate this further, we show a partial grotrian diagram for V in figure 7.1.

In figure 7.1, we have omitted fine structure. There are many other things we can learn from the program. One is that terms of different configurations overlap. This shows that in this case, the CFA is not a good approximation. The angular part of the electrostatic repulsion between electrons is to strong to treat as a perturbation with great accuracy. Nevertheless, the *LS*-coupling notation is still pertinent, but the assignment of the quantum numbers should be seen as what the leading term is in a superposition. Most of the terms in the diagram are strongly mixed.

As pointed out earlier, we are not able to dedicate parent terms in the 3d^{3}4s^2, and this is also the case for 3d^5. For the 3d^{4}4s-configuration, there is first a term given for the 3d^4 configuration in the positive vanadium ion, and to that a 4s-electron is added. For 3d^{3}4s4p we identify two parent terms — one for 3d^3 and one for 4s4p.

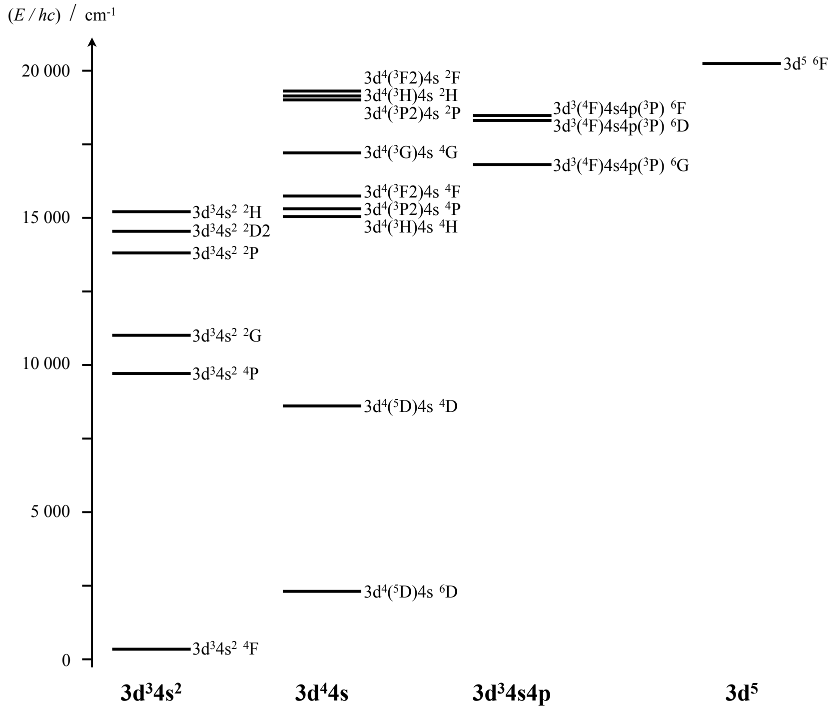


Fig. 7.1 no fine structure, no odd/even

7.1.3 Energies of *LS*-coupling terms

Calculating absolute energies within the CFA is a daunting task, and for the radial part one frequently resorts to heavy numerical calculations (see chapter 14). What we will do in this section is to look specifically at the energy contribution that arises when we apply perturbation theory in order to compute relative energies of *LS*-coupling terms.

If we consider a certain configuration of electrons in open shells, this is specified of a set of quantum numbers n_i and l_i. This leaves a number of possibilities for m_{li} and m_{si}. If there is only one orbital outside filled shells that is populated, there is place for $N_\mathrm{o} = 2(2l-1)$ electrons. If the number of (equivalent) electrons in the orbital is N_v, the number of ways that these can be arranged is:

$$\frac{N_\mathrm{o}!}{N_\mathrm{v}!(N_\mathrm{o}-N_\mathrm{v})!} \ . \tag{7.2}$$

Theses possibilities correspond to combinations of the different m_{li} and m_{si}, exactly as was shown in the tables in chapter 6.3 and also in table 7.3.

All such table entries correspond to unique wave functions that are degenerate in energy in the zero-order approximation — they all belong to the same configuration within the CFA. This means that the perturbation theory has to be of the degenerate kind, and that in order to determine energy contributions relatively large secular problems have to be solved. If we take the d^3-configuration in table 7.3 as an example, the first order energy correction can be found by taking the matrix element of the perturbation Hamiltonian for the Slater determinant that holds all permutations of electron coordinates between all spin-orbital entries in table 7.3 — 120 terms for the complete version of the table.

Solving secular problems of as high dimensions as 120 or higher is a daunting task, but it can be greatly facilitated. Fist of all because the perturbation is diagonal in M_L and M_S, and secondly by using the sum-diagonal rule for matrices. We will look at the former of these simplifications first.

The degeneracy in M_L and M_S is a consequence of the fact that the operators L_z and S_z commute with the Hamiltonian, as long as the spin-orbit coupling is ignored. We can then consider the matrix element of the commutation relation, for example between L_z and the Hamiltonian, between two spin-orbital wave functions, such as the entries in table 7.3.

$$\left\langle \{m_{li}, m_{si}\}' \,|\, [L_z, H] \,|\, \{m_{li}, m_{si}\} \right\rangle = \left\langle M_L' M_S' \,|\, [L_z, H] \,|\, M_L M_S \right\rangle = 0 \,. \tag{7.3}$$

The states $|M_L M_S\rangle$ are eigenvectors to L_z, with eigenvalue M_L, so (7.4) reduces to:

$$(M_L' - M_L)\, H_{M_L' M_S' : M_L M_S} = 0 \,, \tag{7.4}$$

where $H_{M_L' M_S' : M_L M_S}$ is the matrix element of the Hamiltonian between two states $|M_L' M_S'\rangle$ and $|M_L M_S\rangle$. Thus, the only elements of the secular problem that will be non-zero are this for which $M_L' = M_L'$. Exactly the same argument will be valid for S_z and M_S.

The fact that we only have to retain terms that are diagonal in M_L and M_S means that the for the example with d^3, we will, instead of a secular problem with dimension 120, have 36 separate ones, where no one is of higher dimension than eight. If we take a p^2-configuration as an other example (see table 6.3), a 15-dimensional quest is reduced to 11 separate secular equation, with no higher dimension than three.

Determinants as large as 3×3, or 8×8, can still be cumbersome. However, the general mathematical theorem that the the sum of diagonal elements in a square matrix always equal the sum of the eigenvalues means the we typically only need to solve integrals for single wavefunctions, and the determinants we still have to take on are of low dimensions. We will illustrate this in a way introduced by Slater.

Table 7.4 is essentially the same as table 6.3, except that the spin-orbital expressions have been replaced by the corresponding terms. The way to understand the table is that although we have 15 different spin-orbitals, there will only be three energies — the ones corresponding to ^{1}S, ^{3}P and ^{1}D. Nine eigenvalues will be de-

Table 7.4 ghghhghgh

p^2		M_S		
		1	0	-1
M_L	2		^{1}D	
	1	^{3}P	^{3}P , ^{1}D	^{3}P
	0	^{3}P	^{1}S , ^{3}P , ^{1}D	^{3}P
	-1	^{3}P	^{3}P , ^{1}D	^{3}P
	-2		^{1}D	

generate and will all give the energy of the ^{3}P-term. Five will have the energy of ^{1}D, and just one will have the non-degenerate energy of ^{1}S.

We can start by solving the integral for $M_L = 2$ and $M_S = 0$. The actual procedure for the integration will be explained in next section. For the moment, we just assume that we can compute single wavefunction integrals. We have:

$$E_{2,0} = \left\langle (1^+,1^-)\,|H|\,(1^+,1^-)\right\rangle = \langle 2,0\,|H|\,2,0\rangle = E_{^1\mathrm{D}} \,. \tag{7.5}$$

Here, the numbers in the first subscript, and also in the second matrix element, are the values of M_L and M_S respectively. In the first matrix element, we instead use the spin-orbitals, represented as in table 6.3. The state $|\,2,0\,\rangle$ must be one of the five that has the energy of ^{1}D, which means that we can determine the latter by solving a single integral.

To find the energy on the term ^{3}P, we can use the fact that there are six occurrences in table 7.4 where ^{3}P appears alone. This means that also the energy $E_{^3\mathrm{P}}$ can be found with help of one integral. For example,

$$E_{^3\mathrm{P}} = E_{1,1} = \left\langle (1^+,0^+)\,|H|\,(1^+,1^+)\right\rangle \,. \tag{7.6}$$

The final remaining term, ^{1}S can only be found in one place in the table, namely for $M_L = 0$, $M_S = 0$. For those values, we have a cubic secular problem, but two of the eigenvalues have already been found. The diagonal sum rule says that:

$$\begin{aligned} &E_{^1\mathrm{S}} + E_{^3\mathrm{P}} + E_{^1\mathrm{D}} \\ &\qquad = \left\langle (1^+,-1^-)\,|H|\,(0^+,1^0)\right\rangle + \left\langle (0^+,0^-)\,|H|\,(0^+,0^-)\right\rangle \\ &\qquad\qquad + \left\langle (-1^+,1^-)\,|H|\,(-1^+,1^-)\right\rangle \,. \end{aligned} \tag{7.7}$$

As a consequence, we can get the final energy by solving three integrals, and we have completed the task in hand without having to solve any secular problems, let alone one of dimension 15.

There are cases where the diagonal sum rule does not work all the way, but it will always simplify matters considerably. As an example where one determinant cannot be avoided, we will look again at the d^3-configuration, treated in table 7.3. We know that there are seven different terms, ^{2}H, ^{2}G, ^{4}F, ^{2}F, ^{2}D, ^{4}P and ^{2}P, with ^{2}D appearing twice. We accordingly have eight energies to compute. This is illustrated in table 7.5.

Table 7.5 ghghhghgh

p^2		M_S			
		3/2	1/2	-1/2	-3/2
M_L	5		^{2}H	^{2}H	
	4		^{2}G , ^{2}H	^{2}G , ^{2}H	
	3	^{4}F	^{2}F , ^{4}F , ^{2}G , ^{2}H	^{2}F , ^{4}F , ^{2}G , ^{2}H	^{4}F
	2	^{4}F	^{2}D1 , ^{2}D2 , ^{2}F ^{4}F , ^{2}G , ^{2}H	^{2}D1 , ^{2}D2 , ^{2}F ^{4}F , ^{2}G , ^{2}H	^{4}F
	1	^{4}P ^{4}F	^{2}P , ^{4}P , ^{2}D1 , ^{2}D2 ^{2}F , ^{4}F , ^{2}G , ^{2}H	^{2}P , ^{4}P , ^{2}D1 , ^{2}D2 ^{2}F , ^{4}F , ^{2}G , ^{2}H	^{4}P ^{4}F
	0	^{4}P ^{4}F	^{2}P , ^{4}P , ^{2}D1 , ^{2}D2 ^{2}F , ^{4}F , ^{2}G , ^{2}H	^{2}P , ^{4}P , ^{2}D1 , ^{2}D2 ^{2}F , ^{4}F , ^{2}G , ^{2}H	^{4}P ^{4}F
	-1	^{4}P ^{4}F	^{2}P , ^{4}P , ^{2}D1 , ^{2}D2 ^{2}F , ^{4}F , ^{2}G , ^{2}H	^{2}P , ^{4}P , ^{2}D1 , ^{2}D2 ^{2}F , ^{4}F , ^{2}G , ^{2}H	^{4}P ^{4}F
	-2	^{4}F	^{2}D1 , ^{2}D2 , ^{2}F ^{4}F , ^{2}G , ^{2}H	^{2}D1 , ^{2}D2 , ^{2}F ^{4}F , ^{2}G , ^{2}H	^{4}F
	-3	^{4}F	^{2}F , ^{4}F , ^{2}G , ^{2}H	^{2}F , ^{4}F , ^{2}G , ^{2}H	^{4}F
	-4		^{2}G , ^{2}H	^{2}G , ^{2}H	
	-5		^{2}H	^{2}H	

With single matrix elements, we can calculate $E_{^2\mathrm{H}}$ and $E_{^4\mathrm{F}}$. The former together with the diagonal sum rule helps us to get $E_{^2\mathrm{G}}$. The three we have then helps us to calculate $E_{^2\mathrm{F}}$. However, when we get to the terms present for $M_L = 2$, $M_S = 1/2$, we have a secular problem of dimension six, but we have only managed to predetermine four eigenvalues. To proceed, we will have to diagonalise the remaining matrix in order to find $E_{^2\mathrm{D1}}$ and $E_{^2\mathrm{D2}}$, but it is only quadratic. When that is done, we can obtain the remaining two energies, $E_{^4\mathrm{P}}$ and $E_{^2\mathrm{P}}$, with the sum rule.